# Synthesis of fibrous silica tantalum (FSTa) for photooxidative desulphurization

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# Synthesis of fibrous silica tantalum (FSTa) for photooxidative desulphurization

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**Abstract.** The photooxidative desulphurization (PODS) of dibenzothiophene (DBT) was examined under visible light using fibrous silica tantalum (FSTa), tantalum oxide doped fibrous silica (Ta/KCC-1) and commercial tantalum oxide ($Ta_2O_5$). FSTa was synthetized using hydrothermal method, while Ta/KCC-1 was obtained via a wet impregnation method. The catalysts were examined by field emission scanning electron microscopy (FESEM), X-ray Diffraction (XRD) and UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS). It was shown that the FSTa possesses the highest photocatalytic performance (70.2%), due to its fibrous structure, well-dispersion of Ta, as well as its narrower band gap. These traits impact on the photocatalysis by promoting the deposition of the DBT on the catalyst, allowing the efficient transfer of charge carrier and preventing the electron-hole recombination.

## 1. Introduction

Sulphur oxides ($SO_x$) produced from the burning of fossil fuels has causes major impacts on the environment and human health. The emission of $SO_x$ has led to atmospheric acidification, acidic deposition and aerosol production [1]. Thus, moving to low-sulfur fuels is an efficient approach to reduce $SO_x$ emissions which has become a priority for many researchers and industries worldwide. Therefore, different desulphurization methods have been implemented to solve these issues throughout these years [2]. However, among all the treatment technologies, oxidative desulphurization (ODS) is considered as the most suitable technique to obtain an ultra-low sulphur containing in fuel oils due to its low cost, environmentally safe, low temperature and ambient pressure operating condition [3-7]. In order to improve the efficiency of this process, some assistance is often used like adsorptive-, microwave-, extractive-, electrochemical-, ultrasound- and photocatalytic-ODS (PODS).

In recent years, among the different heterogeneous catalysts, $Ta_2O_5$ is ranked as one of the most important transition metal oxides due to its suitable physical, chemical and photocatalytic properties [8]. However, its application under visible light is limited by high band gap energy ($\geq$3.0 eV) which is more active toward UV light irradiation. With this in mind, visible light photocatalysts ($\lambda$= 400–800 nm) is crucial to be implemented for the practical use of PODS, hence, an optimum band-gap (< 3.0 eV) is required [9]. Previous studies have reported many techniques to improve photocatalyst to be used under visible light including the combination with other organic and/or inorganic compounds, addition of support material, incorporation of two or more suitable semiconductors, and the creation of defect structure for improved charge-carrier separation [2]. Besides, surface defect and fibrous morphology might also increase the visible light absorption by reducing the band gap energy [10]. Taking into consideration all the above-mentioned factors, this study aims to synthetize fibrous silica tantalum (FSTa) with narrow band gap and compare its photo activity over Ta/KCC-1 and commercial $Ta_2O_5$ for the PODS of DBT in model oil under visible light.

## 2. Experimental

### *2.1. Material*
Cetyltrimethylammonium bromide (CTAB), urea, butanol, toluene, tetraethyl orthosilicate (TEOS), and dibenzothiophene were purchased from Merck Sdn.Bhd., Malaysia. Tantalum pentoxide ($Ta_2O_5$) were bought from Sigma Aldrich. Acetonitrile and hexane were obtained from QRec, Malaysia.

### *2.2. Catalysts synthesis*
FSTa was prepared using the hydrothermal method as reported by previous work [11]. During synthesis of KCC-1, CTAB and urea were dissolved in distilled water. This solution was then mixed with other separated solution consisting TEOS, toluene and butanol, and stirred homogeneously under heating at 403 K. After cooled, the mixture was centrifuged and dried before being calcined at 823 K for 6 h. For FSTa, a similar procedure was used, except the $Ta_2O_5$ powder was added in the second solution. Ta/KCC-1 was synthesized using a wet impregnation method. Firstly, 1 g of KCC-1 was mixed with water in a beaker and stirred for 5 min, followed by addition of appropriate amount commercial $Ta_2O_5$. The mixture was continuously stirred and heated at 80°C until the fine powder obtained. The powder product was oven-dried for overnight and finally heat treated at 550°C for 3 hours. For $Ta_2O_5$ catalyst, commercial $Ta_2O_5$ was calcined at the same temperature and time as above.

### *2.3. Characterization*
FESEM (JEOL JSM-6701F, Japan) was used to study the morphological properties of the catalysts. The X-ray diffraction (XRD) recorded on Bruker Advance D8, 40 kV, 40 mA powder diffractometer was utilized to investigate the structural properties of the catalysts. The PIKE Technologies DiffusIR was employed to obtain UV–Vis diffuse reflectance spectra (UV –Vis DRS) in the range of 200 to 800 nm for band gap energy measurement.

### *2.4. Photocatalytic oxidative desulphurization reaction*
The photoactivities of the FSTa catalyst was investigated through the PODS of DBT. During reaction, a batch reactor containing 4 visible lamps and a chiller was used. 100 mg $L^{-1}$DBT was dissolved in hexane and used as model oil. Appropriate amount of catalyst was added to the mixed solution consisting model oil and acetonitrile as extractant (ratio 2:1), stirred constantly, and placed in the dark for 30 min to allow complete adsorption–desorption process. After that, the solution was visible light-illuminated and sampling for every 10 min. The sample was centrifuged and analyzed by UV-Vis spectrophotometer (Thermo Scientific Genesys10uv Scanning) at $\lambda$= 326 nm. Each set of experiments was repeated three times to ensure the accuracy. The same procedure was applied for other catalysts.

## 3. Results and discussion

### *3.1. Morphological study.*
The morphology of FSTa was studied using FESEM as shown in Figure 1. It could be noticed from Figure 1A the presence of uniform cockscomb-like spherical shape of FSTa with dendrimeric fibers at its outer surface, with the size varies between 400-650nm (Figure 1B). This structure could offer a high adsorption of DBT molecule towards the catalyst and facilitate the absorption of light for enhanced photoactivity [12].

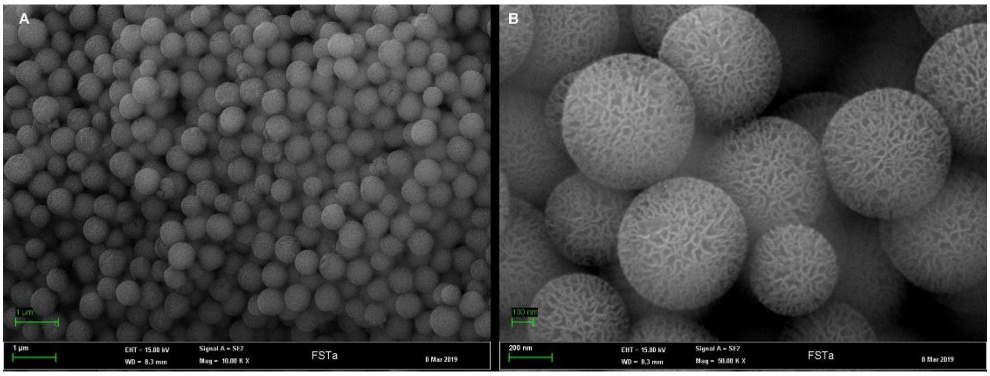


**Figure 1.** FESEM images of FSTa

*3.2. Crystallinity. phase and structural studies.*

XRD patterns of FSTa, Ta/KCC-1 and $Ta_2O_5$ catalysts are displayed in Figure 2. The commercial $Ta_2O_5$ (inset figure) presents a series of different major characteristic peaks at 2θ=22.9, 28.3, 36.7, 46.8, 49.8 and 55.5°. In fact, the FSTa exhibits the main peaks of $Ta_2O_5$ with a lower-intensity and noisy pattern, suggesting that $Ta_2O_5$ is barely losing its structural integrity [13]. This might be due to the presence of dendrimeric silica fibers surrounding the $Ta_2O_5$ seed. The highest intensity observed for the FSTa catalyst, implying the presence of larger $Ta_2O_5$ crystallites in the catalyst [14].

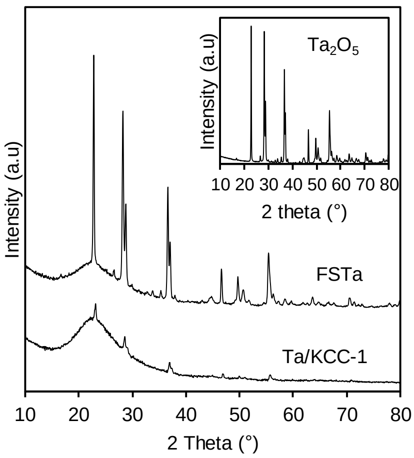


**Figure 2.** XRD patterns of FSTa, Ta/KCC-1 and $Ta_2O_5$ catalysts

*3.3. Optical studies.*

The UV –Vis DRS spectra and calculated band gap of the catalysts are displayed respectively in Figure 3 and Table 1. It could be observed that both Ta/KCC-1 and FSTa demonstrated narrowed band gap which are 2.88 and 2.25 eV, respectively. This is one of the factor to consider for a PODS under visible light. As expected, commercial $Ta_2O_5$ exhibits a wide band gap (3.54 eV) which is much higher than the maximum band gap required for visible light reaction. It is believed that the improved absorption edge may lead to a better charge carrier separation and high harvesting rate of solar light, which subsequently resulted in an enhanced performance.

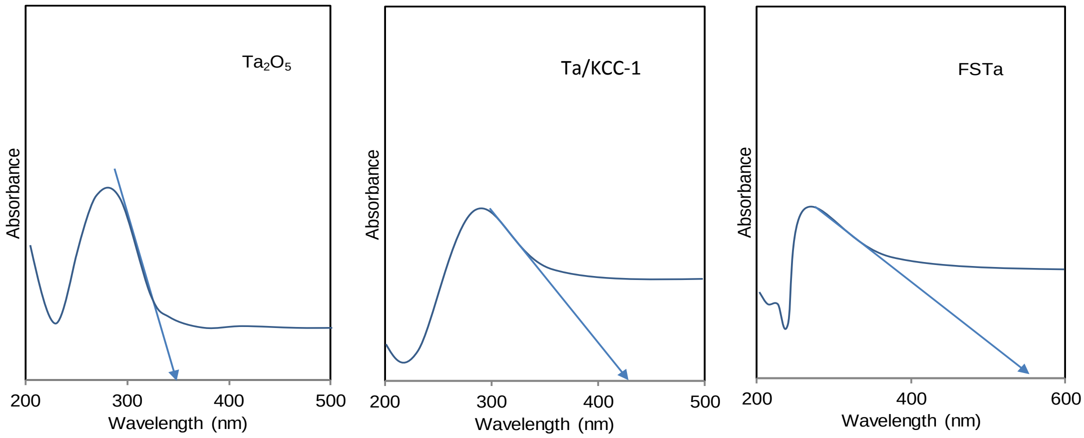


**Figure 3.** UV-Vis spectra of the composites

**Table 1.** Band gap energy of the catalysts

| **Catalyst** | **$E_g$ (eV)** |
|---|---|
| $Ta_2O_5$ | 3.54 |
| Ta/KCC-1 | 2.88 |
| FSTa | 2.25 |

*3.4. Photocatalytic oxidative desulfurization performance*

The photocatalytic performance of the different catalysts was examined in the oxidation of DBT in model oil and their performance is shown in Figure 4.

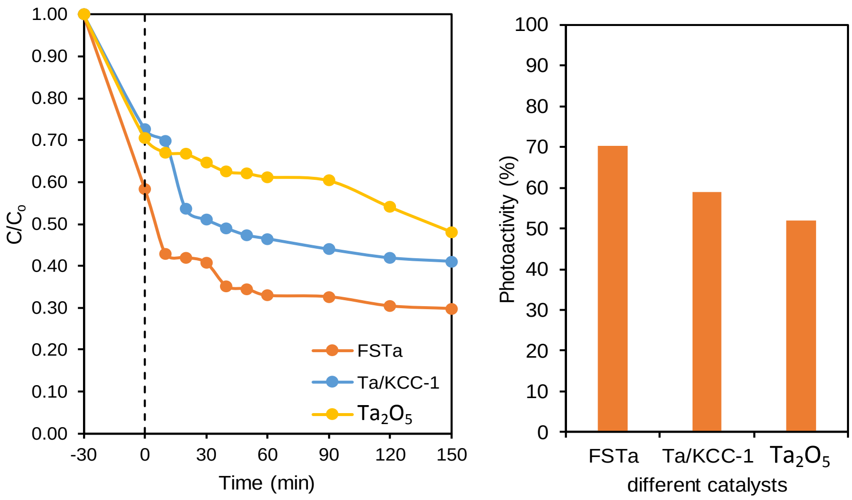


**Figure 4.** Photocatalytic oxidative desulphurization performance of the different catalysts [0.5 g $L^{-1}$ catalyst, 100 mg $L^{-1}$ DBT, 150 min].

It is clearly observed that the FSTa exhibited a better performance compared to Ta/KCC-1 and commercial $Ta_2O_5$ under visible light, and the PODS were in the following order: FSTa (70.2%) > Ta/KCC-1 (58.9%) > commercial $Ta_2O_5$ (51.9%). As predicted earlier, the superior performance demonstrated by FSTa was definitely due to its fibrous morphology for enhanced adsorption of DBT and absorption of visible light, structural completeness with higher crystallinity, well-dispersion of Ta, and narrowest band gap. These criteria might symbiotically play role in preventing the charge recombination for enhanced performance.

## 4. Conclusion

In summary, FSTa was successfully synthesized using a hydrothermal method, and has been successfully used for PODS of DBT under visible light irradiation. A cockscomb-like spherical shape with dendrimeric fibers and size ranging 400-650 nm of FSTa was detected via FESEM analysis. The XRD pattern proves the successfully loading of $Ta_2O_5$ on the surface of the FSTa and Ta/KCC-1 catalyst, in which a better dispersion was observed in FSTa. UV Vis DRS reveals the extended light absorption of both FSTa and Ta/KCC-1 towards visible region, which resulted in narrower band gap as compared to commercial $Ta_2O_5$. The fibrous morphology, well-dispersion of $Ta_2O_5$, as well as the narrowest band gap has allowed the best performance of FSTa than that of other catalysts. These criteria are crucial to improve DBT adsorption and light absorption, prevent the electron-hole recombination, and enhanced photocatalytic performance under visible light irradiation.

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